Time-resolved structural evolution of supercooled barium disilicate liquid during in-situ crystallization

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Abstract

The homogeneous and congruent crystallization of the barium disilicate (BaSi2O5) glass makes it possible to trace the temporal evolution of Raman bands from their positions within the supercooled liquid to those in the crystalline phase. As a result, a detailed structural evolution is revealed during crystallization. The *in-situ* crystallization of supercooled liquid BaSi2O5 at 790∘C has been monitored for over 400 minutes revealing a three-stage crystallization process. Stage 1 involves changes in the barium sites toward a bonding environment that is similar to the ninefold site in the low barium disilicate phase, sanbornite. The end of stage 1 is marked by the loss of a Q4 species vibration at 1170 cm-1 and the new presence of a vibrational band at 440 cm-1, which marks the beginning of stage 2. This behavior may be explained by the degradation of the Q4 site to form highly distorted bridging oxygen sites producing the 440 cm-1 band. Stage 2 is also marked by strong shifts in the bridging oxygen modes at 540 and 575 cm-1 towards their crystal-like positions and relative intensities. This stage is also marked by the transition of the Q3 peak, at 1060 cm-1, from a Gaussian-like to a Lorentzian curve, indicating the formation of well-developed sheet structures. The final stage involves subtle movements of the barium and bridging oxygen sites, and a rapid decrease in the remaining Qn species to form Q3. These structural changes involve the entire silicate network on the tens of microns scale. The observation that barium atoms drive the initial stages of crystallization provides direct evidence that the short-range order around the network modifier is a critical factor involved in homogeneous crystallization.

Keywords: glass, crystallization, barium disilicate, supercooled liquid, crystal growth, silicate, structure, Raman spectroscopy

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